

# PATENT SPECIFICATION

781,594

Inventor :—ROBERT LIONEL SAMUEL.

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F4(A : E : F : G : K)

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## COMPLETE SPECIFICATION.

### A Process for Coating Metals.

We, DIFFUSION ALLOYS LIMITED, a British Company, of 18 Maddox Street, London, W.1, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement :—

This invention relates to a process for coating a metal with a coating containing chromium.

Various processes have been described for coating one metal with another metal wherein the metal to be coated is heated in the presence of a gaseous halide of another metal.

In many cases it would be an advantage to have available a process whereby the metal surface can be coated with the active compound prior to treatment and heat subsequently applied.

The present invention provides a process for coating a metal with a coating containing chromium by diffusion wherein the metal to be coated is first coated with a liquid or pasty composition containing the chromium or chromium alloy in powder form, together with a carrier which is solid at room temperature but becomes liquid or begins to melt at the operating temperature, and which is a halide other than a chromium halide, whereafter the coated metal is heated by high frequency heating until diffusion of the chromium takes place.

This composition may also, if desired, contain a bonding agent which will ensure that the composition is liquid or pasty when applied to the metal surface, but solidifies into a sufficiently hard coating after a short time to allow for a convenient handling prior to the thermal treatment.

Examples of carriers which may be used are cryolite alkali metal or alkaline earth

metal fluorides, chlorides, bromides and iodides, for example fluorspar, potassium iodide or barium chloride. The use of cryolite has been found to be particularly suitable when the operating temperature is within the range of 900 to 1300° C.

The bonding agent should be chosen according to the temperature requirements. Organic silicates, for example ethyl silicate, are very suitable as they hydrolyse quickly with the formation of a hard silica cement. Other bonding agents which may be employed are solutions of cellulose esters and ethers, such as cellulose acetate, where quick drying is required, or organic colloidal substances, such as glue or gelatine, where slow drying is required.

Complex silicates, such as Portland cement can be added in small quantities.

The metal to be coated may be, for example, aluminium, copper, cobalt, iron, nickel, molybdenum, tungsten or titanium. The coating contains chromium but may also contain other metals such as aluminium, copper, cadmium, iron, manganese, molybdenum, titanium, vanadium, tungsten, zirconium, silicon, nickel or cobalt.

It will be understood that the term "metal" as used herein includes alloys and also includes silicon.

Ferrous metals, such as iron and steel, and nickel, copper, and titanium are of particular importance as metals to be coated.

After the metal to be coated has been treated with the composition referred to above, the heating is effected by high frequency heating which may be effected in an induction furnace or by means of a high-frequency inductor.

If the composition is not entirely impervious to oxidising gases, or if uncoated

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parts of metallic articles under treatment have to be subjected to heat, atmosphere-controlled furnaces may be used or gas-tight retorts or boxes and in some cases salt-bath furnaces, provided in the latter instance that there is no appreciable interaction between the composition and the molten salt.

The following examples illustrate the invention:—

#### EXAMPLE 1.

An internal combustion engine sparking plug made of EN.17 medium carbon steel (cf. B.S. 970:1947) was taken and the threaded end was coated with a composition consisting of cryolite, a mixture of metal powders consisting of 90% of chromium powder and 10% of aluminium powder, and a solution of ethyl silicate in alcohol. After the alcohol had evaporated the threaded end of the plug with the coating thereon was introduced into the central area of a small high-frequency inductor coil and current applied for seventy seconds. The surface temperature was estimated to be 1200° C. The composition then flaked off easily and micro-etching showed a clear zone of chromium-aluminium rich alloy of approximately 0.0025" in depth. This zone was resistant to dilute nitric acid and to oxidation at elevated temperature.

#### EXAMPLE 2.

A molybdenum rod 2" long and  $\frac{1}{2}$ " in diameter was coated with a composition consisting of fluorspar, chromium powder and gelatine dispersed in water. The molybdenum rod was then introduced into a glass tube, closed at one end, approximately  $1\frac{1}{2}$ " in diameter and a few crystals of ammonium iodide were introduced into the tube. The open end of the tube was heated in a blow-pipe and drawn to a very fine opening. Heat was applied at the bottom of the tube to volatilise the ammonium iodide and expel the air. The function of the ammonium iodide is thus to expel the air and provide further halide for the process. The tube was then placed in the centre of a high frequency inductor and current applied. Heating for a few seconds with a surface temperature of about 1400° C. provided a substantial chromium alloy coating having a high resistance to thermal oxidation.

The process of the present invention has the advantages of speed of operation, and the possibility of localised treatment.

Our Specification No. 718,095 claims a process for coating a metal with chromium by diffusion wherein an article of the metal to be

treated is coated with a mixture containing chromium or an alloy thereof, preferably in a finely powdered condition, a halide, preferably an ammonium halide or an alkali or alkaline earth halide, and a bonding substance; or with a salt, preferably a halide, of chromium and a bonding substance and the coated article is then heated to a temperature sufficiently high to effect diffusion of the chromium into the article.

The term "bonding substance" is defined in Specification No. 718,095 as meaning kaolin, alumina, magnesia, powdered refractory, silica, inorganic silicates, organic silicates, gelatine, organic compounds of the "glue" type, collodion and cellulose acetate.

What we claim is:—

1. A process for coating a metal with a coating containing chromium by diffusion wherein the metal to be coated is first coated with a liquid or pasty composition containing the chromium or chromium alloy in powder form, together with a carrier which is solid at room temperature but becomes liquid or begins to melt at the operating temperature, and which is a halide other than a chromium halide; whereafter the coated metal is heated by high frequency heating until diffusion of the chromium takes place.

2. A process as claimed in Claim 1 wherein the composition also contains a bonding agent.

3. A process as claimed in Claim 2 wherein the bonding agent is an organic silicate, e.g. ethyl silicate.

4. A process as claimed in any one of the preceding claims wherein the carrier is an alkali metal or alkaline earth metal fluoride, chloride, bromide or iodide.

5. A process as claimed in any one of the preceding Claims 1 to 3 wherein the carrier is cryolite.

6. A process as claimed in any one of the preceding claims wherein the metal to be coated is a ferrous metal.

7. A process for coating a metal with a coating containing chromium substantially as described with reference to either of the examples.

8. Coated metals when obtained by the process claimed in any one of the preceding claims.

ELKINGTON & FIFE.

Consulting Chemists and Chartered Patent Agents.

Bank Chambers, 329 High Holborn,  
London, W.C.1.

Agents for the Applicants.

## PROVISIONAL SPECIFICATION.

## A Process for Coating Metals.

We, DIFFUSION ALLOYS LIMITED, a British Company, of 18 Maddox Street, London, W.1 do hereby declare this invention to be described in the following statement:—

5 This invention relates to a process for coating one metal with another metal.

Various processes have been described for coating one metal with another metal wherein the metal to be coated is heated in the presence of a gaseous halide or another metal.

10 In many cases it would be an advantage to have available a process whereby the metal surface can be coated with the active compound prior to treatment and heat subsequently applied by induction furnace or high frequency inductor.

The present invention provides a process for coating one metal with another metal by diffusion wherein the metal to be coated is first coated with a liquid or pasty composition containing the diffusing metal or metals in powder form, together with a carrier which is solid at room temperature but becomes liquid or begins to melt at the operating temperature, and which is a metal halide other than a halide of the coating metal; whereafter the coated metal is heated until diffusion of the diffusing metal takes place.

20 This composition may also, if desired, contain a bonding agent which will ensure that the composition is liquid or pasty when applied to the metal surface, but solidifies into a sufficiently hard coating after a short time to allow for a convenient handling prior to the thermal treatment.

35 Examples of carriers which may be used are alkali metal or alkaline earth metal fluorides, bromides, iodides, and complex compounds of the same, for example fluorspar, cryolite, potassium iodide or barium chloride. The use of cryolite has been found to be particularly suitable when the operating temperature is within the range of 900 to 1300° C.

45 The bonding agent should be chosen according to the temperature requirements. Organic silicates, for example ethyl silicate, are very suitable as they hydrolyse quickly with the formation of a hard silica cement. Other bonding agents which may be employed are solutions of cellulose esters and ethers, such as cellulose acetate, where quick drying is required, or organic colloidal substances, such as glue or gelatine, where slow drying is required.

50 Complex silicates, such as Portland cement, can be added in small quantities in certain cases.

The metal to be coated may be, for example, aluminium, copper, cobalt, iron, nickel, molybdenum, tungsten or titanium, and the diffusing metal may be aluminium, chromium, copper, cadmium, iron, manganese, molybdenum, titanium, vanadium, tungsten, zirconium, silicon, nickel or cobalt.

60 It will be understood that the term "metal" as used herein includes alloys and also includes silicon.

Ferrous metals, such as iron and steel, nickel, copper, and titanium are of particular importance as metals to be coated.

70 After the metal to be coated has been treated with the composition referred to above, the heating may be effected in an induction furnace or by means of a high-frequency inductor.

If the composition is not entirely impervious to oxidising gases, or if uncoated parts of metallic articles under treatment have to be subjected to heat, atmosphere-controlled furnaces may be used or gas-tight retorts or boxes and in some cases salt-bath furnaces, provided in the latter instance that there is no appreciable interaction between the composition and the molten salt.

85 The following examples illustrate the invention:—

1. An internal combustion engine sparking plug made of EN.17 medium carbon steel was taken and the threaded end was coated with a composition consisting of cryolite, a mixture of metal powders consisting of 90% of chromium powder and 10% of aluminium powder, and a solution of ethyl silicate in alcohol. After the alcohol had evaporated the threaded end of the plug with the coating thereon was introduced into the central area of a small high-frequency inductor coil and current applied for seventy seconds. The surface temperature was estimated to be 1200° C. The composition then flaked off easily and micro-etching showed a clear zone of chromium-aluminium rich alloy of approximately 0.0025" in depth. This zone was resistant to dilute nitric acid and to oxidation at elevated temperature.

2. A molybdenum rod 2" long and  $\frac{1}{8}$ " in diameter was coated with a composition consisting of fluorspar, chromium powder and gelatin dispersed in water. The molybdenum rod was then introduced into a glass tube, closed at one end, approximately 1 $\frac{1}{2}$ " in diameter and a few crystals of ammonium iodide were introduced into the tube. The open end of the tube was heated in a blow-pipe and drawn to a very fine opening. Heat

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was applied at the bottom of the tube to volatilise the ammonium iodide and expel the air. The tube was then placed in the centre of a high-frequency inductor and current applied. Heating for a few seconds with a surface temperature of about 1400° C. provided a substantial chromium alloy coating having a high resistance to thermal oxidation.

10 The process of the present invention has

the advantages of speed of operation, and the possibility of localised treatment.

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Bank Chambers, 329 High Holborn.  
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Agents for the Applicants. *WD*

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